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Brief Reports

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Short- and long-range interactions of slow electrons in condensed matter: Effects on reflection and transmission

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The Coulomb interaction of an electron with each electron or nucleus in its environment is Fourier analyzed into components with wave vectors **q**. These components are classified as long (short) range when q is smaller (larger) than the electron's wave number p. The contrasting characteristics of each class are discussed. Electron reflection at a material's surface measures the effect of short-range components only.

A recent note has introduced the study of the motion and of the energy degradation of "subexcitation electrons" whose energy does not suffice to produce electronic excitations of a material.[1] These electrons nevertheless dissipate any energy in excess of $k_B T$ by exciting the motion of atomic nuclei in their environment. We consider condensed-matter environments that are macroscopically homogeneous and isotropic, typically liquids or solids in which the correlations of atomic structure extend no further than a few atomic diameters. More specifically, the range of these correlations should not exceed the wavelength of the electron of interest, because longer-range correlations would present additional problems. Reference 1 showed that the penetration, degradation, and diffusion of electrons in such homogeneous materials may be treated by the same stochastic analysis in the subexcitation range as at higher energies.

Here I deal with the relevance of the electron wavelength, which exceeds the size of atoms at energies much lower than 1 Ry (13.6 eV). A long wavelength largely suppresses the electron's correlations with the atomic structure of a homogeneous material. This lack of correlation is manifested by the large mean free path of slow electrons, which exceeds atomic diameters by an order of magnitude.[2] Correlations develop instead readily over distances larger than the electron's wavelength, typically through electric polarization of the material that surrounds a subexcitation electron. Contrasting circumstances thus influence the Coulomb interaction of a subexcitation electron with its environment, depending on whether a specific electron or nucleus in the medium lies within or without the electron's wavelength.

This remark suggests treating the effects of short- and long-range interactions *separately*. The homogeneity of the materials of interest suggests further that this separation be performed through the Fourier representation of interactions, such as is performed operationally in the structure analysis by diffraction.[3] The Coulomb interaction of a subexcitation electron at a point $\mathbf{r}$ with a particle of the material having charge $z_j e$ at the point $\mathbf{r}_j$ has the integral representation

$$\begin{aligned} V(\mathbf{r}-\mathbf{r}_j) &= z_j e^2 / |\mathbf{r}-\mathbf{r}_j| \\ &= 4\pi z_j e^2 \int d\mathbf{q}\, q^{-2} \exp[i\mathbf{q}\cdot(\mathbf{r}_j-\mathbf{r})] \ . \end{aligned} \tag{1}$$

[We consider here separately the subexcitation electron's interaction with *each* electron or nucleus; the contributions of individual particles are then combined in Eq. (2).] Long- (short-) range components of V can thus be classified by values of q smaller (larger) than the electron's momentum $\mathbf{p}$ (in units of $\hbar$). The matrix element of $\sum_j V(\mathbf{r}-\mathbf{r}_j)$, between states n and n' of the material and electron states with momenta $\mathbf{p}$ and $\mathbf{p}'$, factors out in the form

$$\begin{aligned} &\left(n'\mathbf{p}' \left| \sum_j z_j V(\mathbf{r}-\mathbf{r}_j) \right| n\mathbf{p} \right) \\ &\qquad = \frac{e^2}{2\pi^2 q^2} \left(n' \left| \sum_j \exp(i\mathbf{q}\cdot\mathbf{r}_j) \right| n \right) \delta(\mathbf{p}-\mathbf{q}-\mathbf{p}') \ . \end{aligned} \tag{2}$$

The matrix element $(n' | \sum_j z_j \exp(i\mathbf{q}\cdot\mathbf{r}_j) | n)$ of a material measures its ability to absorb a momentum $\mathbf{q}$, whether in a transition $n \rightarrow n'$ or while remaining in a state $n \equiv n'$. This important parameter is often called a "form factor" of the material and is indicated by $F_{n'n}(\mathbf{q})$; isotropy of the material implies that its form factors are independent of the direction of $\mathbf{q}$.

Long-range (i.e., low-q) components of this interaction amount to dielectric polarization of the material, whose effects are familiar and accessible to evaluation by perturbation treatment. They include inelastic transitions which excite rovibrational—mostly optically active—modes of the material, since the analogous electron excitations are inaccessible to subexcitation electrons. The resulting rate of energy dissipation is a linear function of the imaginary part of the reciprocal dielectric function, $\mathrm{Im}[-1/\epsilon(\omega)]$, as it is also for fast electrons.[4] The elastic components of the polarization consist of *virtual* excitations of rovibrational *and* electronic modes together with their reaction on the electron itself. The combination of the electron with the surrounding cloud of polarization is called a "polaron." Restricting this combination to Fourier components with $q < p$ characterizes it as a "small polaron" and validates its treatment by perturbation theory.[5] The polarization cloud does not contribute to the polaron's momentum $\mathbf{p}$ but shifts its energy eigenvalue E to a level generally lower than that of an electron with momentum $\mathbf{p}$ in the absence of polarization. The dependence of E on p determines the polaron's effective mass $m^* = (d^2E/dp^2)^{-1}$. The eigenvalue E includes an imaginary part, $-i\gamma/2$, which represents the rate of energy dissipation through thermalization of rovibronic excitations.

Describing and evaluating the net effect of short-range interactions of a subexcitation electron presents a greater challenge because large momentum transfers lift this electron to an infinite range of virtual states with momenta $p' = |\mathbf{p}-\mathbf{q}| \gg p$. It is the superposition of a large set of such transitions—each of them made unlikely by large nonconservation of energy—that smooths out the combined effect of high q interactions, thus suppressing correlations of the electron with its environment. The net effect of short-range interactions is presumably approximated by a constant ("optical") potential which shifts the energy of a slow electron with respect to its value in vacuum. This shift combines with the shift induced by the polarization cloud, to yield the electron affinity of the material, which is equivalently represented as an "extraction potential" or, more precisely, as the difference between the zero-momentum energies of an electron in vacuum and in the material. The zero-momentum energy level of an electron in condensed matter is often referred to as the "bottom of the conduction band."

Early efforts have been made to quantify the optical potential for nonpolar substances with complete valence shells, such as condensed noble gases or methane, mainly by extrapolating its value from the gas phase.[6] This value is proportional to the density of molecules n and to the scattering length a of electron-molecule elastic collisions, being represented simply by $2\pi na$ in atomic units.[7] (The scattering length is replaced, for nonzero values of the electron momentum, by a combination of p and of the s-wave phase shift, $a \rightarrow p^{-1}\sin\delta_0$.[8]) The scattering length of gas molecules includes an important contribution of long-range polarization which even reverses the sign of a for Ar, Kr, and Xe but should be treated *separately* in our approach, thus bypassing recent arguments on its subject.[9] After separating this polarization effect, the evaluation of the effective scattering length still appears far from straightforward according to Ref. 6(b).

The analysis and evaluation of the net effect of short-range interactions should meet additional complications in the presence of polar molecules—typically in aqueous solutions—and especially in amorphous substances with unfilled open shells. In amorphous semiconductors electrons can be trapped in "Anderson localized" empty orbitals lying in the energy gap below the conduction band of the valence shell. Molecular substances with unfilled valence states, such as those with double-bonded carbon chains, can similarly hold an electron permanently or temporarily in unoccupied orbitals, thus affording atypical examples of strong correlations between subexcitation electrons and molecular structures. The example of transient electron capture by condensed N_2 molecules has been studied experimentally,[10] leading to the discovery of a novel contribution to electron degradation dubbed "dielectric hysteresis."[11] This multifaceted outline of the effects of short-range electron interactions indicates that the next stage of their study should be spearheaded by experimentation.

An opportunity to sort out experimentally the contributions of short- and long-range interactions is afforded by measurements of electron reflection and refraction coefficients at the surface of a material, complemented by measurements of the transmission through thin layers.[12] Recall that reflection and refraction in optics stem from the structural discontinuity of materials at their surfaces. They hinge, more specifically, on the gradient of the refractive index being sharper than the gradient of the radiation fields. In the context of this note the effective sharpness of an electron's entry into a material depends on the *spectrum of its interaction's wave vectors* $\mathbf{q}$ (more precisely on the spectrum of their components $q_\perp$ orthogonal to the surface) rather than on the far sharper discontinuity of matter density. Reflection and refraction of electrons at a surface are represented by rapid changes of the orthogonal component $p_\perp$ of the electron's momentum $\mathbf{p}$. Such changes can *only* stem from *short-range interaction* components with $q > p$.

On the other hand, polaron formation proceeds gradually as an electron approaches and then traverses the surface of a material. Its influence on the electron's motion can be treated semiclassically and consists of a progressive variation, generally an increase, of the orthogonal momentum component $p_\perp$. (The component $p_\parallel$ parallel to the surface remains constant, of course, insofar as the surface is flat.) The polaron formation as an electron approaches the surface of a conductor is familiarly schematized by the electron's approach to its "image."

Testing and sharpening this outline of slow electron passage through the surface of a material appears to be within the scope of the experimental techniques of Refs. 2, 10, and 12. Even though the orthogonal component $p_\perp$ of the incident momentum seems most relevant to reflection in contrast to the parallel component, the influence of *both* parameters should be assessed by experimental control of the energy and incidence of the electron. The magnitude and direction of **p** *within* a crystalline material might also be accessible to observation through interferences depending on the material's thickness.[13] Information might also be gleaned by observing an electron after it reemerges from the material.

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